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The final technical report summarizes our development on the methodology to study the structure and dynamics of highly branched epoxy polymers. We have made advances in providing new approaches to this complex problem. Unfortunately, the project was not renewed for further studies.

During the contract period, we have developed the methodology to study the structure and dynamics of epoxy polymer formation by using laser light scattering intensity and linewidth measurements, small angle x-ray scattering with a synchrotron x-ray source and chemical analysis. We have also tried to approach the kinetics and mechanisms of the epoxy copolymerization reaction by using the Smoluchowski coagulation equation.

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Laser Scattering Studies of Epoxy Polymerization Processes

Final Report

Ben Chu

November 4, 1988

U.S. Army Research Office

Contract #DAAG29-85-K-0067

Chemistry Department

State University of New York at Stony Brook

I. FOREWORD

The research project deals with studies of structure, dynamics and polymerization processes of epoxy polymer formation using mainly scattering techniques. During the project period, we were concerned with (1) the application of Raman and laser light scattering to the melt as well as solution polymerization of hexachlorocyclotriphosphazene, a precursor for most polyphosphazene inorganic elastomers. We divided the epoxy studies first into several sub-areas because of our anticipation in the complexities associated with a more fundamental understanding of the structure and dynamics of epoxy polymers, especially during the initial stages of branched polymer formation before the gelation threshold. The investigations include (2) structure and dynamics of entangled polymer coils in solution, and (3) characterization of non-spherical particle size distributions. Finally, with the completion of small-angle x-ray scattering (SAXS) instrumentation at the X21A State University of New York (SUNY) beam line, the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), we were able to make SAXS studies on (4) the fractal geometry in epoxy polymerization processes.

I.1. Application of Raman and Light Scattering to the Melt and Solution Polymerization of Hexachlorocyclotriphosphazene

Poly(dichlorophosphazene) (PDP) can be synthesized by either thermal polymerization of melt hexachlorocyclotriphosphazene (HCTP) or solution polymerization of HCTP in various solvents. A combination of Raman spectroscopy, angular measurements of absolute light scattering intensities and Rayleigh linewidth (dynamic) light scattering measurements were employed to develop an on-line monitoring technique in characterizing the degree of polymerization, the molecular weight, the molecular weight distribution, the radius of gyration, as well as intermolecular interactions, in terms of the

second virial coefficients and the cooperative diffusion coefficient of the polymer product (PDP) formed. The development of the Raman/light scattering spectroscopic methodology in characterizing PDP in situ avoids the decomposition of PDP by moisture and has been adapted at the Materials Technology Laboratory (Watertown, Mass.) to investigate the polymerization processes of HCTP under a variety of conditions.

I.2. Structure and Dynamics of Entangled Polymer Coils in Solution

Entangled polymer coils in solution form temporary networks which have similar structure as permanent covalent-bounded polymer networks. When the translational motions of probe polymer coils are much faster than coil disentanglement motions in the polymer matrix, the structure and dynamics of probe polymer coils in semidilute solutions will help us to understand how polymer molecules move in polymer networks. In studying the polymer probe structure and dynamics, we used a liquid mixture of two organic solvents, toluene and α-chloronaphthalene, which could be made isorefractive with the polystyrene (PS) matrix and studied how polymethylmethacrylate (PMMA) probe coils of known molecular weights and sizes, such as the radius of gyration (R_g), could move in the pseudo (temporary) polymer network of mesh size (ξ) with $\xi < R_g$, $\xi \sim R_g$ and $\xi > R_g$. By varying the composition of the solvent mixture, we could also study the entanglement structure in terms of ξ and dynamics of the PS matrix in terms of the corresponding cooperative diffusion coefficient. Such an approach can then be transferred to investigate polymer coil motions during epoxy network formation.

I.3. Characterization of Non-spherical Particle Size Distributions

We have combined transient electric birefringence (TEB) yielding information on rotational diffusion coefficients with laser light scattering (LLS) in order to obtain additional information on the average particle shape of each fraction of sizes (based on translational diffusion

coefficients) from Laplace inversion of the measured net intensity-intensity time correlation function. Although epoxy polymer networks are essentially symmetric, the purpose of combining the two techniques is to be able to develop a possible experimental approach for studying the behavior of polymer composites using suspended anisotropic particles (or molecules) in the matrix during epoxy polymerization processes. We have also examined the coupling of diffusive motions for large thin disks.

I.4. Fractal Geometry in Epoxy Polymerization Processes.

A modified Kratky small-angle x-ray scattering (SAXS) goniometer has been adapted successfully to the X21A SUNY beam line at NSLS/BNL. The concept of fractal geometry can be applied to investigate cured epoxy systems. The fractal concept has shown to be a useful approach to describe the structure of random systems, such as aggregates of colloidal silica, branched silica condensation polymers, cross-linked poly(dimethyl-siloxane), aggregating proteins and gold colloids, as well as diffusion-limited polymerization of the conducting polymer polypyrrole and other growth processes, e.g., pecolation and cluster-cluster aggregation. The fractal dimension d_f of a branched epoxy polymer was determined before its gelation threshold. By combining SAXS with LLS, we have a direct method to experimentally determine the molecular weight and the molecular weight distribution of branched epoxy polymer during its curing process.

In the latter period of the project, we became interested in the kinetics and mechanisms of copolymerization of epoxy resins with an anhydride, with or without a catalyst. With our light and x-ray scattering techniques, we find that our data, obtained from the curing of 1,4-butanediol diglycidyl ether (DGEB) with cis-1,2-cyclohexane-dicarboxylic anhydride (CH), in the presence of benzyl dimethyl amine (CA) as a catalyst, can best be fitted by the zeroth-order reaction. However, it is not crucial

for us to know how the reaction is initiated if we focus our attention mainly to the branching kinetics, and the structure and dynamics of branched epoxy polymer products during different stages of the copolymerization reaction process.

We investigated (5) the branching kinetics of the copolymerization reaction based on the Smoluchowski coagulation equation, (6) the determination of molecular weight distribution of branched epoxy polymers based on Brownian dynamics and (7) the characterization of structural inhomogeneities based on the Debye-Bueche theory.

I.5. Branching Kinetics

The branching kinetics of the copolymerization reaction and the distribution of highly branched epoxy copolymers can be approached using the concept of Smoluchowski's coagulation equation. The equation has been applied to study the structure of clusters produced by the kinetic aggregation of colloidal particles. If we take the overall branching probability $w(i,j)$ to be proportional to the sum of active sites on the two polymers, i.e. $w(i,j) \propto (i+j)$ where i and j are the active sites on polymers i and j, respectively, the kinetic equation can be solved explicitly to obtain the weight-average molecular weight (M_w) and the molecular weight distribution (MWD) at different reaction stages.

I.6. Molecular Weight Distribution of Specific Highly Branched Epoxy Polymers

The molecular weight distribution (MWD) of the branched epoxy polymer formed during each reaction stage can be estimated by means of dynamic light scattering. The procedure is as follows. Estimates of the normalized characteristic linewidth (Γ) distribution function, $G(\Gamma)$, can be obtained from the measured intensity-intensity time correlation function, $G^{(2)}(\tau)$, by using the Laplace inversion. $G(\Gamma)$ can then be transformed to the molecular

weight distribution by incorporating information based on the static and dynamic properties of the branched epoxy polymer solution, i.e., the weight-average molecular weight (M_w), the second virial coefficient (A_2), the z-average root-mean-square radius of gyration (R_g), the diffusion second virial coefficient (k_d), the z-average translational diffusion coefficient at infinite dilution ($\overline{D}_o^o$), and the scaling relation $D_o^o = k_D M^{-\alpha_D}$. Knowledge gained from laser light scattering (LLS) of our broad MWD epoxy polymers is sufficient to calibrate the size exclusion chromatographic (SEC) column for specific branched epoxy polymer studies.

I.7. Optical Inhomogeneities of Epoxy Melts

The laser light scattering intensity envelope in the presence of different amounts of catalyst at different temperatures (e.g., 60, 70, 80 and 90°C) can be analyzed according to the Debye-Bueche theory. The intensity of light scattered by an inhomogeneous medium is dependent upon the local refractive index difference in the inhomogeneous medium in terms of the mean square average of local dielectric constant fluctuations $\overline{\eta^2}$ which can be related to structural changes during the copolymerization process. The comparison between experiments and theoretical models can provide a useful framework for the assumptions and approximations which are needed to find a solution for the Smoluchowski coagulation equation.

FINAL REPORT

Statement of the Problem

1. Determination of M_w, R_g, A_2, $\bar{D}^o_o$, and MWD of the DGEB/CH epoxy system in the presence of CA during the copolymerization reaction before the gelation threshold.
2. Study of the internal structure of epoxy polymers by means of the fractal concept using SAXS at NSLS/BNL.
3. Application of the Smoluchowski coagulation equation to investigate the branching kinetics and mechanisms of the DGEB/CH system.

Summary of Most Important Results

I. We have developed a new method to estimate MWD of highly branched epoxy polymers by combining dynamic light scattering (DLS) with size exclusion chromatography.

II. A modified Kratky SAXS gomiometer was adapted at the SUNY X21A2 Beamline to study the fractal dimension of epoxy polymers.

III. The application of scattering techniques (DLS, SAXS, etc.) to the copolymerization reaction of an epoxy resin/anhydride system permits us to monitor the macromolecular parameters during various stages of the polymerization reaction process.

IV. The Smoluchowski coagulation equation provides a new approach to examine the kinetics and mechanisms of epoxy copolymerization processes.

List of all Publications and Technical Papers Presented Discussed in I.1- .

A. Publications with acknowledgement of support by the U.S. Army Research Office

1. B. Chu, Light Scattering Studies of Polymer Solution Dynamics, <u>J. Polymer Sci., Polymer Symp.</u>, <u>73</u>, 137 (1985).
2. Day-chyuan Lee, James R. Ford, George Fytas, Benjamin Chu and Gary L. Hagnauer, "Application of Raman and Laser Light Scattering to the Melt Polymerization of Hexachlorocyclotriphosphazene. I." <u>Macromolecules</u>, <u>19</u>, 1586 (1986).
3. Benjamin Chu and Day-chyuan Lee, "Application of Laser Light Scattering to Solution Polymerization of Hexachlorocyclotri-phosphazene. II." <u>Macromolecules</u>, <u>19</u>, 1592 (1986).
4. Benjamin Chu, Dan-qing Wu and Guo-mei Liang, "Polymer Probe Dynamics", <u>Macromolecules</u>, Communication, <u>19</u>, 2665 (1986).
5. H.S. Dhadwal and B. Chu, "Fiber Optics in Laser Light Scattering Spectroscopy," <u>J. Coll. & Interface Sci.</u>, Note, <u>115</u>, 561 (1987).
6. Zukang Zhou, Yannis Georgalis, Wenping Liang, Jialin Li, Renliang Xu and Benjamin Chu, "Colloidal Behavior of Cobalt Monooleate Soap in Apolar Organic Solvents," <u>Journal of Colloid and Interface Science</u>, <u>116</u>, 473 (1987).
7. Renliang Xu, James R. Ford and Benjamin Chu, "Photon Correlation Spectroscopy, Transient Electric Birefringence and Characterization of Particle Size Distributions in Colloidal Suspensions," <u>in</u> ACS Symposium Series No. 332, Particle Size Distribution: Assessment and Characterization, Theodore Provder, ed., Chap. 8, 1987, pp. 115-132.

8. Renliang Xu and Benjamin Chu, "Dynamic Light Scattering of Thin Disks: Coupling of Diffusive Motions", Journal of Colloid & Interface Science, 117, 22 (1987)

9. Benjamin Chu and Dan-Qing Wu, "Polymer Probe Dynamics," Macromolecules, 20, 1606 (1987).

10. Benjamin Chu, "Laser Light Scattering" in Determination of Molecular Weight, edited by A.R. Cooper, John Wiley & Sons, N.Y., Vol. 103, Chemical Analysis Series, in press.

11. Benjamin Chu, D.-Q. Wu and C. Wu, "A Kratky Block-Collimation Small Angle X-Ray Diffractometer for Synchrotron Radiation," Rev. Sci. Instrum., 58, 1158 (1987).

12. Benjamin Chu, Chi Wu, Dan-Qing Wu and James Phillips, "Fractal Geometry in Branched Epoxy Polymer Kinetics," Macromolecules, Communication, 20, 2642 (1987).

13. Benjamin Chu and Chi Wu, "Structure and Dynamics of Epoxy Polymers," Macromolecules, 21, 1729 (1988).

14. Benjamin Chu, Renliang Xu, Tadakazu Maeda and Harbans S. Dhadwal, "A Prism Laser Light Scattering Spectrometer," Rev. Sci. Instrum., 59, 716 (1988).

15. Chi Wu, Ju Zuo and Benjamin Chu, "Molecular Weight Distribution of a Branched Epoxy Polymer: 1,4-Butanediol Diglycidyl Ether with Cis-1,2-Cyclohexanedicarboxylic Anhydride," Macromolecules, in press.

16. Chi Wu, Ju Zuo and Benjamin Chu, "Laser Light Scattering Studies of Epoxy Polymerization of 1,4-Butanediol Diglycidyl Ether with Cis-1,2-Cyclohexanedicarboxylic Anhydride," Macromolecules, in press.

17. Benjamin Chu, Renliang Xu and Zhulun Wang, "Low-Field Transient Electric Birefringence of DNA in Agarose Gels," Biopolymers, Communication, in press.

B. Papers presented with acknowledgement of support by the U.S. Army Research Office (* denotes abstract or preprint)

1985 *1. American Chemical Society Meeting, Chicago, Illinois. Symposium on The Assessment of Particle Size Distributions. Photon Correlation Spectroscopy, Transient Electric Birefringence and Characterization of Particle Size Distributions in Colloidal Suspensions, by Renliang Xu, James R. Ford and Benjamin Chu. (Invited speaker)

2. ZIF Conference on From Simple to Complex Liquids, Bielefeld, Germany. Structure and Dynamics of Polymer Solutions and Melts, by Benjamin Chu. (Invited speaker and session chairman)

*3. 1985 Scientific Conference on Chemical Defense Research, Aberdeen Proving Ground, Maryland. Structure and Dynamics of Multicomponent Polymer Solutions in Semidilute Regimes, by Benjamin Chu, Dan-Qing Wu and Guo-Mei Liang. Proceedings, CRDC-SP-86007, 579 (1986).

4. 1985 AIChE Annual Meeting, Chicago, Illinois. Light Scattering and Characterization of Poly(Dichlorophosphazene) During Thermal Polymerization, by D.C. Lee, J.R. Ford, B. Chu, M. Sennett and G.L. Hagnauer. (Talk presented by D.C. Lee).

1986 *5. American Chemical Society Meeting, New York City. Symposium on Reversible Polymeric Gels. Structure and Dynamics of Multicomponent Solutions in Semidilute Regimes, by Benjamin

Chu, Dan-Qing Wu and Guo-Mei Liang. (Invited speaker). Polymer Preprints, 27, 219 (1986).

*6. American Chemical Society Meeting, New York City. Symposium on Advances in Size Exclusion Chromatography. Characterization of Branched Polyvinyl Acetate by Light Scattering, Gel Permeation Chromatography and Viscometry, by I.H. Park, Q.-W. Wang and B. Chu. (Paper presented by Q.-W. Wang).

7. Conference on Quasi-Elastic Light Scattering Spectra - Ideas and Interpretations, Worcester, Massachusetts. Polymer Probe Dynamics, by Benjamin Chu and Dan-Qing Wu. (Invited speaker).

*8. 1986 Scientific Conference on Chemical Defense Research, Aberdeen Proving Ground, Maryland. Supramolecular Formation and Creation of Non-Newtonian Fluids, by Benjamin Chu and Zukang Zhou. (Invited speaker).

1987 *9. American Chemical Society Meeting, Denver, Colorado. Light Scattering Studies of Polymer Diffusion in Semidilute Solutions, by Benjamin Chu, Dan-Qing Wu, Qin-Wei Wang and Zhulun Wang. (Invited speaker). Polymer Preprints, 28, 336 (1987).

*10. Nagoya Meeting on Pattern Formation, Nagoya, Japan. Fractal Structure of Silica Aggregates and Epoxy Branched Polymers. (Invited lecturer and discussion leader.)

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